



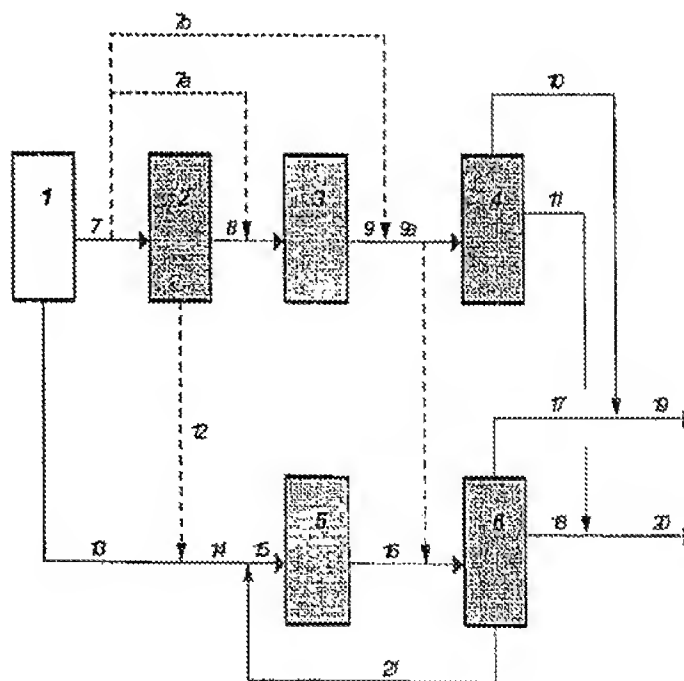
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : C10L 1/08, C10G 65/14, 2/00, C10L 1/16		A1	(11) International Publication Number: WO 00/60029
			(43) International Publication Date: 12 October 2000 (12.10.00)
(21) International Application Number: PCT/ZA99/00147		(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 23 December 1999 (23.12.99)			
(30) Priority Data: 60/128,036 6 April 1999 (06.04.99) US 99/02789 19 April 1999 (19.04.99) ZA			
(71) Applicant (for all designated States except US): SASOL TECHNOLOGY (PTY) LTD [ZA/ZA]; 1 Sturdee Avenue, Rosebank, 2196 Johannesburg (ZA).			
(72) Inventor; and (75) Inventor/Applicant (for US only): DANCUART, Luis, Pablo [ZA/ZA]; 20 Lombard Street, Vaalpark, 9570 Sasolburg (ZA).			
(74) Agents: HAHN, Hans, H. et al.; Hahn & Hahn Inc., 222 Richard Street, Hatfield, 0083 Pretoria (ZA).			
		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: PROCESS FOR PRODUCING SYNTHETIC NAPHTHA FUEL AND SYNTHETIC NAPHTHA FUEL PRODUCED BY THAT PROCESS

## (57) Abstract

The invention provides a process for the production of a synthetic naphtha fuel suitable for use in compression ignition (CI) engines, the process including at least the steps of hydrotreating at least a fraction of a Fischer-Tropsch (FT) synthesis reaction product of CO and H<sub>2</sub>, or a derivative thereof, hydrocracking at least a fraction of the FT synthesis product or a derivative thereof, and fractionating the process products to obtain a desired synthetic naphtha fuel characteristic. The invention also provides a synthetic naphtha fuel made by the process as well as a fuel composition and a Cloud Point depressant for a diesel containing fuel composition, said fuel composition and said depressant including the synthetic naphtha of the invention.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LB	Liberia	SG	Singapore		

## Process for Producing Synthetic Naphtha Fuel and Synthetic Naphtha Fuel Produced by that Process

This invention relates to naphtha fuels useable in Compression Ignition (CI) combustion engines as well as to a process for production of such naphtha fuels. More particularly, this invention relates to naphtha fuels produced from a mainly paraffinic synthetic crude which is produced by the reaction of CO and H<sub>2</sub>, typically by the Fischer-Tropsch (FT) process.

### Background to the invention

Products of a FT hydrocarbon synthesis process, particularly the products of a cobalt and/or iron based catalytic process, contain a high proportion of normal paraffins. Primary FT products provide notoriously poor cold flow properties, making such products difficult to use where cold flow properties are vital, e.g. diesel fuels, lube oil bases and jet fuel. It is known in the art that octane number and cetane number are normally inversely related i.e. a higher octane number is typically associated with a lower cetane number. It is also known that naphtha fractions intrinsically have low cold flow characteristics like congealing and cloud points. There is thus an incentive for a process to produce a synthetic naphtha fuel obtained from the FT process which has good cold flow characteristics and a Cetane number compatible with CI engine fuel requirements. Additionally, such synthetic naphtha fuel may have acceptable biodegradability properties.

The synthetic naphtha fuel described in this invention is produced from a paraffinic synthetic crude (syncrude) obtained from synthesis gas (syngas) through a reaction like the FT reaction. The FT primary products cover a broad range of hydrocarbons from methane to species with molecular masses above 1400; including mainly paraffinic hydrocarbons and smaller quantities of other species such as olefins, and oxygenates.

The prior art teaches in US 5,378,348 that by hydrotreating and isomerizing the products from a Fisher-Tropsch reactor one can obtain a jet fuel with freezing point of -34°C or lower due to the iso-paraffinic nature of this fuel. This increased product branching relative to the waxy paraffin feed corresponds with a Cetane rating (combustion) value less than that for normal (linear) paraffins, depicting that an increase in branching reduces the Cetane value of paraffinic hydrocarbon fuels.

Surprisingly, it has now been found by the applicant, that a hydroprocessed synthetic naphtha fuel may be produced having a Cetane number, typically in excess of 30, as well as good cold flow properties. The synthetic naphtha fuels of the present invention could be used on their own or in blends in CI

engines, typically where diesel fuels are presently used. This would lead to the more stringent fuel quality and emission specifications being satisfied. The synthetic naphtha fuels of the present invention may be blended with conventional diesel fuels to have lower emissions, good cold flow characteristics, low aromatics content and acceptable cetane numbers.

5

### Summary of the invention

Thus, according to a first aspect of the invention, there is provided a process for the production of a synthetic naphtha fuel suitable for use in CI engines, the process including at least the steps of:

- 10 a) hydrotreating at least a fraction of a Fischer-Tropsch (FT) synthesis reaction product of CO and H<sub>2</sub>, or a derivative thereof;
- b) hydrocracking at least a fraction of the FT synthesis product or a derivative thereof; and
- c) fractionating the process products to obtain a desired synthetic naphtha fuel characteristic.

- 15 The process may include the additional step of blending the fractionated process products in a desired ratio to obtain a synthetic naphtha fuel having desired characteristics for use in a CI engine.

The process as described above may produce a synthetic naphtha wherein some of the desired characteristics include:

- 20 - having a high Cetane number in excess of 30;
- having a low sulfur content below about 5 ppm;
- having good cold flow properties; and
- having more than 30% isoparaffins, wherein the isoparaffins include methyl and/or ethyl branched isoparaffins.

25

According to yet another aspect of the invention, there is provided a process for producing a synthetic naphtha fuel having a Cetane number higher than 30, the process including:

- (a) separating the products obtained from synthesis gas via the FT synthesis reaction into one or more heavier fraction and one or more lighter fraction;
- 30 (b) catalytically processing the heavier fraction under conditions which yield predominantly distillates;
- (c) separating a naphtha product fraction of step (b) from a heavier product fraction which is also produced in step (b); and
- (d) optionally, blending the naphtha product obtained in step (c) with at least a portion of the one
- 35 or more lighter fraction of step (a), or products thereof.

The catalytic processing of step (b) may be a hydroprocessing step, for example, hydrocracking or mild hydrocracking.

5 The process for producing a synthetic naphtha fuel may include one or more additional step of fractionating at least some of the one or more lighter fraction of step (a), or products thereof, prior to step (d).

The process for producing a synthetic naphtha fuel may include the additional step of hydrotreating at least some of the one or more light fraction of step (a), or products thereof, prior to step (d).

10

The one or more heavier fraction of step (a) may have a true boiling point (TBP) in the range of about 70°C to 700°C, however, it may be in the range 80°C to 650°C.

15

The one or more lighter fraction may have a true boiling point (TBP) in the range -70°C to 350°C, typically in the range -10°C to 340°C.

The product of step (d) may boil in the range 30°C to 200°C. The product of step (d) may boil in the range 40°C to 155°C, as measure by the ASTM D86 method.

20

The product of step (d) may be a naphtha fuel.

The product of step (d) may have a Cloud Point below -30°C, typically -40°C and even below -50°C.

25

The product of step (d) may be obtained by mixing the naphtha product fraction obtained in step (c) with at least a portion of the one or more lighter fraction of step (a), or products thereof, in a volume ratio of between 1:24 and 9:1, typically 2:1 and 6:1, and in one embodiment, in a volume ratio of 50:50.

30

The invention extends further to a process for the production of synthetic naphtha fuels suitable for CI engines, from FT primary products, comprising predominantly short chain linear and branched paraffins.

35

In this process, the waxy product from the FT process is separated into at least two fractions, a heavier and at least one lighter fraction. The lighter fraction may be subjected to mild catalytic hydrogenation to remove hetero-atomic compounds such as oxygen and to saturate olefins, thereby producing material useful as naphtha, diesel, solvents, and/or blending components therefor. The heavier fraction may be catalytically hydroprocessed without prior hydrotreating to produce products with good cold

flow characteristics. This hydroprocessed heavier fraction could be blended with all or part of the hydrogenated and/or unhydrogenated light fraction to obtain, after fractionation, naphtha fuel characterised by an acceptable Cetane number.

- 5 The catalysts suitable for the hydroprocessing steps are commercially available and can be selected towards an improved quality of the desired final product.

According to a further aspect of the invention, there is provided a synthetic naphtha fuel having a Cetane number above 30 and a Cloud Point below  $-30^{\circ}\text{C}$ , said naphtha fuel having an isoparaffinic  
10 content substantially as described above.

In one embodiment, the synthetic naphtha fuel is a FT product.

The invention extends to a fuel composition including from 10% to 100% of a synthetic naphtha fuel  
15 as described above.

Typically, the fuel composition may include from 0 to 90% of one or more diesel fuels.

The fuel composition may include at least 20% of the synthetic naphtha fuel, the composition having a  
20 Cetane number greater than 40 and a Cloud Point below  $2^{\circ}\text{C}$ . Using the synthetic naphtha as Cloud Point depressor may result in at least  $2^{\circ}\text{C}$  depression in Cloud Point of the fuel composition.

The fuel composition may include at least 30% of the synthetic naphtha fuel, the composition having a Cetane number greater than 40 and a Cloud Point below  $0^{\circ}\text{C}$ . Using the synthetic naphtha as Cloud  
25 Point depressor may result in at least  $3^{\circ}\text{C}$  depression in Cloud Point for the fuel composition.

The fuel composition may include at least 50% of the synthetic naphtha fuel, the composition having a Cetane number greater than 40 and a Cloud Point below  $0^{\circ}\text{C}$ , more typically below  $-4^{\circ}\text{C}$ . Using the synthetic naphtha as Cloud Point depressor may result in at least  $4^{\circ}\text{C}$  depression in Cloud Point for the  
30 fuel composition, or more typically at least  $8^{\circ}\text{C}$  depression.

The fuel composition may include at least 70% of the synthetic naphtha fuel, the composition having a Cetane number greater than 40 and a Cloud Point below  $-10^{\circ}\text{C}$ , more typically below  $-15^{\circ}\text{C}$ . Using the synthetic naphtha as Cloud Point depressor may result in at least  $13^{\circ}\text{C}$  depression in Cloud Point  
35 for the fuel composition, or more typically at least  $18^{\circ}\text{C}$  depression.

The blend composition may further include from 0 to 10% additives to improve other fuel characteristics.

5 The additives may include a lubricity improver. The lubricity improver may comprise from 0 to 0.5% of the composition, typically from 0.00001% to 0.05% of the composition. In some embodiments, the lubricity improver comprises from 0.008% to 0.02% of the composition.

10 The fuel composition may include, as the diesel, a crude oil derived diesel, such as US 2-D grade (low sulphur No. 2-D grade for diesel fuel oil as specified in ASTM D 975-94) and/or CARB (California Air Resources Board 1993 specification) diesel fuel, and/or a South African specification commercial diesel fuel.

### Detailed Description

15 This invention describes the conversion of primary FT products into naphtha and middle distillates, for example, naphtha fuels having a Cetane number in excess of 30, while also having good cold flow properties, as described above.

20 The FT process is used industrially to convert synthesis gas, derived from coal, natural gas, biomass or heavy oil streams, into hydrocarbons ranging from methane to species with molecular masses above 1400.

25 While the main products are linear paraffinic materials, other species such as branched paraffins, olefins and oxygenated components may form part of the product slate. The exact product slate depends on reactor configuration, operating conditions and the catalyst that is employed, as is evident from e.g. Catal.Rev.-Sci. Eng., 23(1&2), 265-278 (1981).

30 Preferred reactors for the production of heavier hydrocarbons are slurry bed or tubular fixed bed reactors, while operating conditions are preferably in the range of 160°C – 280°C, in some cases 210-260°C, and 18 – 50 bar, in some cases 20-30 bar.

35 Preferred active metals in the catalyst comprise iron, ruthenium or cobalt. While each catalyst will give its own unique product slate, in all cases the product slate contains some waxy, highly paraffinic material which needs to be further upgraded into usable products. The FT products can be converted into a range of final products, such as middle distillates, naphtha, solvents, lube oil bases, etc. Such conversion, which usually consists of a range of processes such as hydrocracking, hydrotreatment and distillation, can be termed a FT work-up process.

The FT work-up process of this invention uses a feed stream consisting of C<sub>5</sub> and higher hydrocarbons derived from a FT process. This feed is separated into at least two individual fractions, a heavier and at least one lighter fraction. The cut point between the two fractions is preferably less than 300°C and typically around 270°C.

The table below gives a typical composition of the two fractions, with 10% accuracy:

Table 1: Typical Fischer-Tropsch product after separation into two fractions (vol% distilled)

	FT Condensate (< 270°C fraction)	FT Wax (> 270°C fraction)
C <sub>5</sub> -160°C	44	3
160-270°C	43	4
270-370°C	13	25
370-500°C		40
> 500°C		28

The >160°C fraction, contains a considerable amount of hydrocarbon material, which boils higher than the normal naphtha range. The 160°C to 270°C fraction may be regarded as a light diesel fuel. This means that all material heavier than 270°C needs to be converted into lighter materials by means of a catalytic process often referred to as hydroprocessing, for example, hydrocracking.

Catalysts for this step are of the bifunctional type; i.e. they contain sites active for cracking and for hydrogenation. Catalytic metals active for hydrogenation include group VIII noble metals, such as platinum or palladium, or a sulphided Group VIII base metals, e.g. nickel, cobalt, which may or may not include a sulphided Group VI metal, e.g. molybdenum. The support for the metals can be any refractory oxide, such as silica, alumina, titania, zirconia, vanadia and other Group III, IV, VA and VI oxides, alone or in combination with other refractory oxides. Alternatively, the support can partly or totally consist of zeolite. However, for this invention the preferred support is amorphous silica-alumina.

Process conditions for hydrocracking can be varied over a wide range and are usually laboriously chosen after extensive experimentation to optimise the yield of naphtha. In this regard, it is important to note that, as in many chemical reactions, there is a trade-off between conversion and selectivity. A very high conversion will result in a high yield of gases and low yield of naphtha fuels. It is therefore important to painstakingly tune the process conditions in order to optimise the conversion of >160°C

hydrocarbons. Table 2 gives a list of the preferred conditions.

**Table 2: Process conditions for hydrocracking**

CONDITION	BROAD RANGE	PREFERRED RANGE
Temperature, °C	150-450	340-400
Pressure, bar-g	10-200	30-80
Hydrogen Flow Rate, m <sup>3</sup> /m <sup>3</sup> feed	100-2000	800-1600
Conversion of >370°C material, mass %	30 - 80	50 -- 70

Nevertheless, it is possible to convert all the >370°C material in the feedstock by recycling the part that is not converted during the hydrocracking process.

As is evident from table 1, a large proportion of the fraction boiling below 160°C (light condensate) is already in the typical boiling range for naphtha, i.e. 50 - 160°C. This fraction may or may not be subjected to hydrotreating. By hydrotreating, hetero-atoms are removed and unsaturated compounds are hydrogenated. Hydrotreating is a well-known industrial process, catalysed by any catalyst having a hydrogenation function, e.g. Group VIII noble metal or sulphided base metal or Group VI metals, or combinations thereof. Preferred supports are alumina and silica.

Table 3 gives typical operating conditions for the hydrotreating process.

**Table 3: Operating conditions for the hydrotreating process.**

CONDITION	BROAD RANGE	PREFERRED RANGE
Temperature, °C	150-450	200-400
Pressure, bar(g)	10-200	30-80
Hydrogen Flow Rate, m <sup>3</sup> /m <sup>3</sup> feed	100-2000	400-1600

While the hydrotreated fraction may be fractionated into paraffinic materials useful as solvents, the applicant has now surprisingly found that the hydrotreated fraction may be directly blended with the products obtained from hydrocracking the wax. Although it is possible to hydroisomerise the material contained in the condensate stream, the applicant has found that this leads to a small, but significant loss of material in the naphtha boiling range to lighter material. Furthermore, isomerisation leads to the

formation of branched isomers, which leads to Cetane ratings less than that of the corresponding normal paraffins.

Important parameters for a FT work-up process are maximization of product yield, product quality and cost. While the proposed process scheme is simple and therefore cost-effective, it produces synthetic naphtha fuels suitable for CI engines, having a Cetane number  $>30$  in good yield. In fact, the process of this invention is able to produce a naphtha for use in a CI engine of hitherto unmatched quality, which is characterized by a unique combination of both acceptable Cetane number and excellent cold flow properties.

10

It is the unique composition of the synthetic naphtha fuel, which is directly caused by the way in which the FT work-up process of this invention is operated, that leads to the unique characteristics of said fuel.

15 The described FT work-up process of Figure 1 may be combined in a number of configurations. The applicant considers these an exercise in what is known in the art as Process Synthesis Optimisation.

However, the specific process conditions for the Work-up of FT primary products, the possible process configurations of which are outlined in Table 4, were obtained after extensive and laborious experimentation and design.

**Table 4 - Possible Fischer-Tropsch Product Work-up Process Configurations**

Process Step		Process Scheme			
		A	B	C	D
1	FT Synthesis Reactor	X	X	X	X
2	Light FT Product Fractionator	X			
3	Light FT Product Hydrotreater	X	X	X	X
4	Light HT FT Product Fractionator			X	X
5	Waxy FT Product Hydrocracker	X	X	X	X
6	Product Fractionator	X	X	X	X

25	Numbers	reference numerals of Figure 1
	FT	Fischer-Tropsch

The basic process is outlined in the attached Figure 1. The synthesis gas (syngas), a mixture of

Hydrogen and Carbon monoxide, enters the FT reactor 1 where the synthesis gas is converted to hydrocarbons by the FT reaction.

A lighter FT fraction is recovered in line 7, and may or may not pass through fractionator 2 and hydrotreater 3. The product 9 from the hydrotreater may be separated in fractionator 4 or, alternatively, mixed with hydrocracker products 16 sent to a common fractionator 6.

A waxy FT fraction is recovered in line 13 and sent to hydrocracker 5. If fractionation 2 is considered the bottoms cut 12 are to be sent to hydrocracker 5. The products 16, on their own or mixed with the lighter fraction 9a, are separated in fractionator 6.

Depending on the process scheme, a light product fraction, naphtha 19, is obtained from fractionator 6 or by blending equivalent fractions 10 and 17. This is a typically C<sub>5</sub>-160°C fraction useful as naphtha.

A somewhat heavier cut, synthetic diesel 20, is obtainable in a similar way from fractionator 6 or by blending equivalent fractions 11 and 18. This cut is typically recovered as a 160-370°C fraction useful as diesel.

The heavy unconverted material 21 from fractionator 6 is recycled to extinction to hydrocracker 5. Alternatively, the residue may be used for production of synthetic lube oil bases. A small amount of C<sub>1</sub>-C<sub>4</sub> gases are also separated in fractionators 4 and 6.

The following examples 1-9 will serve to illustrate further this invention.

## 25 Nomenclature used in examples

LTFT Low Temperature Fischer-Tropsch. A Fischer-Tropsch synthesis completed at temperatures between 160°C and 280°C, using the basic process conditions as described previously in this patent, at pressures of 18 to 50 bar in a tubular fixed bed or slurry bed reactor.

SR Straight Run. A product obtained directly from LTFT that has not been subjected to any chemical transformation process.

HT SR Hydrogenated Straight Run. A product obtained from LTFT SR products after being hydrogenated using the basic process conditions as described previously in this patent.

HX Hydrocracked. A product obtained from LTFT SR products after being hydrocracked

using the basic process conditions as described previously in this patent.

#### Example 1

- 5 A Straight Run (SR) naphtha was produced by fractionation of the light FT Condensate. This product had the fuel characteristics indicated in Table 5. The same table contains the basic properties of a petroleum based diesel fuel.

#### Example 2

10

A Hydrogenate Straight Run (HT SR) naphtha was produced by hydrotreating and fractionation of the light FT Condensate. This product had the fuel characteristics indicated in Table 5.

#### Example 3

15

A Hydrocracked (HX) naphtha was produced by hydrocracking and fractionation of the heavy FT wax. This product had the fuel characteristics indicated in Table 5.

#### Example 4

20

A LTFT Naphtha was produced by blending of the naphthas described in examples 2 and 3. The blending ratio was 50:50 by volume. This product had the fuel characteristics indicated in Table 5.

**Table 5** Characteristics of the LTFT Naphthas

	Synthetic FT Naphthas				Commercial SA Diesel	Notes
	SR	HT SR	HX	LTFT		
ASTM D86						
IBP, °C	58	60	49	54	182	
T10, °C	94	83	79	81	223	
T50, °C	118	101	101	101	292	
T90, °C	141	120	120	120	358	
FBP, °C	159	133	131	131	382	
Density, kg/L (20°C)	0.7101	0.6825	0.6877	0.6852	0.8483	
Cetane Number	n/a	42,7	30,0	39,6	50,0	
Heat of Combustion, HHV, kJ/kg	45 625	48 075	46 725	46 725	45 520	note 2
Acid Number, mg KOH/g	0.361	0.001	0.011	0.006	0.040	
Total sulphur, mg/L	<1	<1	<1	<1	4 242	
Composition, % wt						
n-paraffins	53,2	90,1	28,6	59,0	n/a	
Iso-paraffins	1,2	8,3	66,7	38,2	n/a	
Naphthenics	-	-	-	-	n/a	
Aromatics	-	0,1	0,5	0,3	n/a	
olefins	35,0	1,5	4,2	2,5	n/a	
alcohols	10,7	-	-	-	n/a	
Cloud Point, °C	-51	-54	-35	-33	4	
Flash Point, °C	-9	-18	-21	-20	57	note 3
Viscosity	n/a	n/a	n/a	0,50	3,97	

Notes: 1. These fuels contain no additives; 2. API Procedure 14A1.3; 3. Correlated (ref.: HP Sep 1987 p. 81)

5

**Example 5**

The SR Naphtha, described in example 1, was tested for emissions obtaining the results indicated in table 6. A Mercedes Benz 407T Diesel engine was used for the test, with the characteristics also indicated in table 6. The emissions measured during the test were 21,6% less CO, 4,7% less CO<sub>2</sub>, and 20,0% less NO<sub>x</sub> than that those measured for the conventional diesel fuel. Additionally, the Particulates emission measured by the Bosch Smoke Number was 52% lower than that observed for the conventional diesel fuel. The specific fuel consumption was 0,2% lower than that observed for the conventional diesel.

15

**Example 6**

The HT SR Naphtha, described in example 2, was tested for emissions obtaining the results indicated in table 6. A Mercedes Benz 407T Diesel engine was used for the test, with the characteristics also indicated in table 6. The emissions measured during the test were 28,8% less CO, 3,5% less CO<sub>2</sub>, and 26,1% less NO<sub>x</sub> than that those measured for the conventional diesel fuel. Additionally, the

20

Particulates emission measured by the Bosch Smoke Number was 45% lower than that observed for the conventional diesel fuel. The specific fuel consumption was 4,9% lower than that observed for the conventional diesel.

#### 5 Example 7

The HX Naphtha, described in example 3, was tested for emissions obtaining the results indicated in table 6. A Mercedes Benz 407T Diesel engine was used for the test, with the characteristics also indicated in table 6. The emissions measured during the test were 7,2% less CO, 0,3% less CO<sub>2</sub>, and  
 10 26,6% less NO<sub>x</sub> than that those measured for the conventional diesel fuel. Additionally, the Particulates emission measured by the Bosch Smoke Number was 54% lower than that observed for the conventional diesel fuel. The specific fuel consumption was 7,1% lower than that observed for the conventional diesel.

#### 15 Example 8

The LTFT Naphtha, described in example 4, was tested for emissions obtaining the results indicated in table 6. An unmodified Mercedes Benz 407T Diesel engine was used for the test, with the characteristics also indicated in table 6. The emissions measured during the test were 25,2% less CO,  
 20 4,4% less CO<sub>2</sub>, and 26,1% less NO<sub>x</sub> than that those measured for the conventional diesel fuel. Additionally, the Particulates emission measured by the Bosch Smoke Number was 45% lower than that observed for the conventional diesel fuel. The specific fuel consumption was 4,6% lower than that observed for the conventional diesel.

25 Table 6 : CI Engine and Emissions Performance of the Synthetic Naphthas

	Synthetic Naphthas				Conventional Diesel
	SR	HT SR	HX	LTFT	
<b>Test Data</b>					
Engine	Mercedes Benz 407T				
Test condition	1 400 rpm				
Load	553 Nm				
<b>Fuel</b>					
Consumption, kg/h	17,55	16,72	16,34	16,77	17,58
<b>Emissions</b>					
CO, g/kWh	0,87	0,79	1,03	0,83	1,11
CO <sub>2</sub> , g/kWh	668,1	676,1	698,9	670,1	700,9
NO <sub>x</sub> , g/kWh	13,59	12,55	12,47	12,55	16,99
<b>Exhaust Smoke</b>					
Bosh Smoke Number	0,32	0,37	0,31	0,37	0,67

**Example 9**

The LTFT Naphtha was blended in a 50:50 proportion (volume) with a commercial South African diesel to produce a fuel suitable for cold weather environments. The fuel characteristics of this fuel and its components are included in Table 7. In Table 8 the performance of this fuel blend, and that of its components, in a Compression Ignition (CI) Engine are shown. The 50:50 blend shows 10% lower specific fuel consumption, 19% lower NO<sub>x</sub> emissions and 21% lower Bosch Smoke Number. Other parameters are also significant.

The commercial diesel fuel is a conventional non-winter fuel grade. Conventionally petroleum refiners producing diesel fuels for cold weather environments are forced to reduce the final boiling points of their products. By doing this, they reduce the cold flow characteristics, making it more compatible with low temperature operation and reducing the possibility of freezing. This results in lower production levels, not only for diesel fuels but also for jet fuel and other products like heating oils.

The blend of the LTFT Naphtha and the commercial South African Diesel is a fuel suitable for cold weather environments that can be prepared without reducing production of conventional fuel. The blend retains the advantages of conventional fuels, including acceptable cetane number and flash points, and can be used in cold conditions without additives or loss of performance. Additionally the blend might have environmental advantages in respect to emissions.

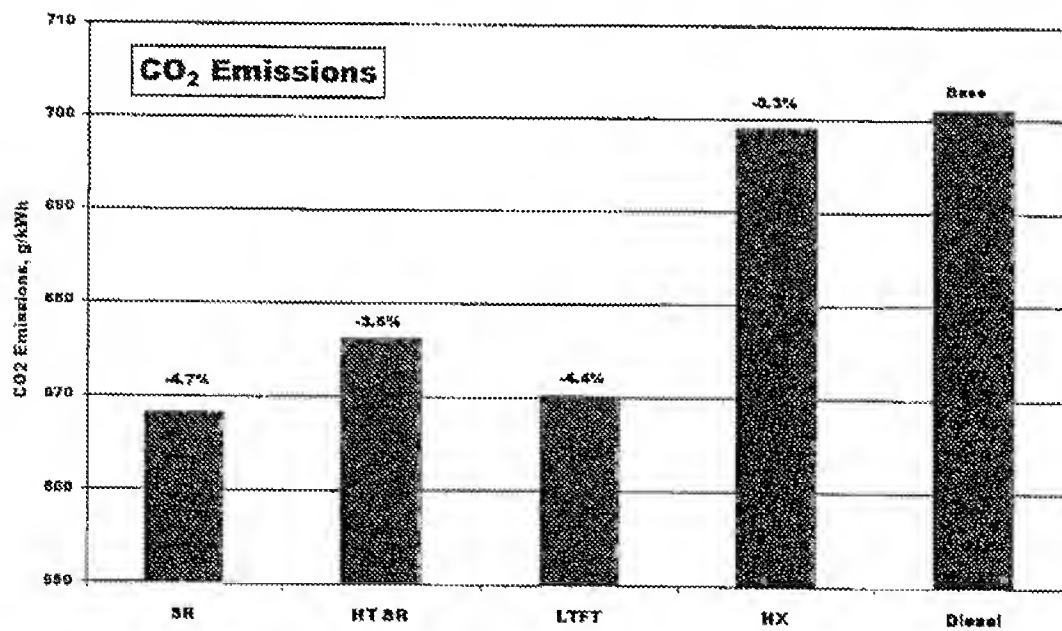
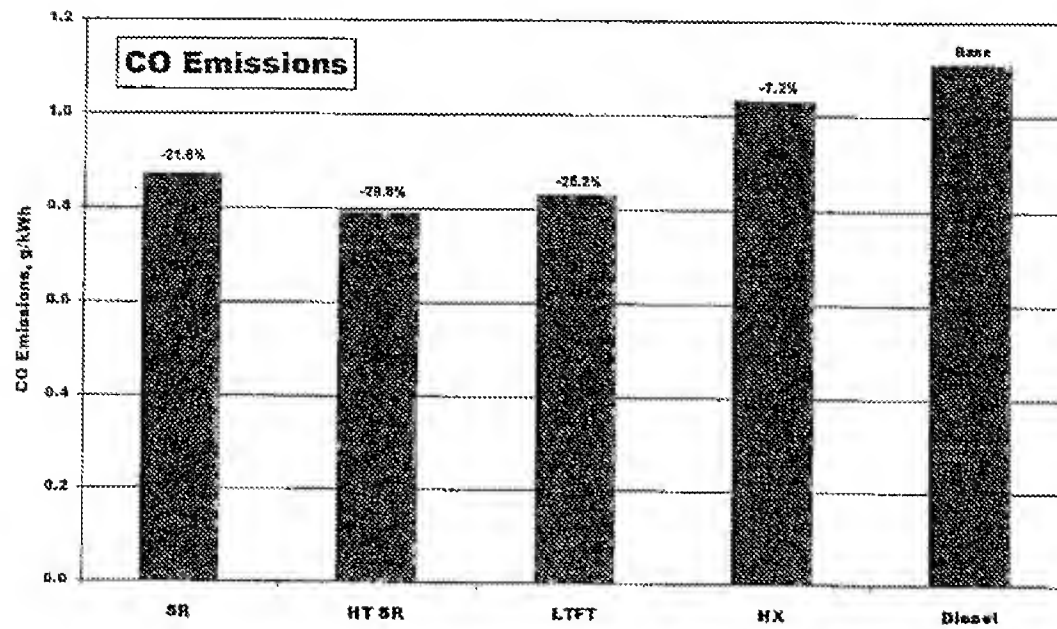
Some of the results included in Tables 7 and 8 are illustrated graphically in the attached figures at the end of the Examples.

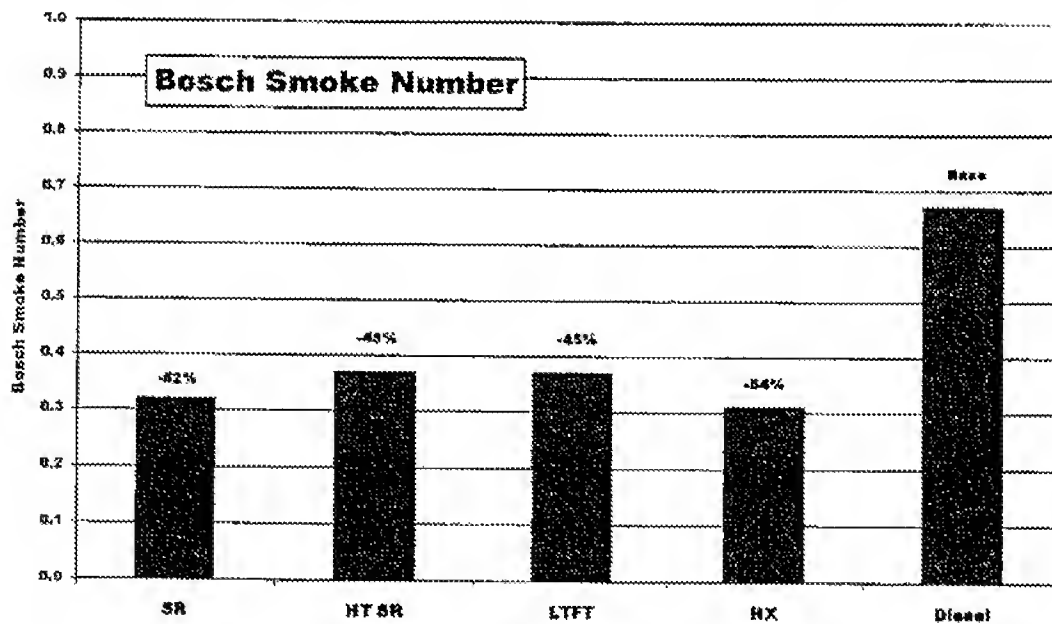
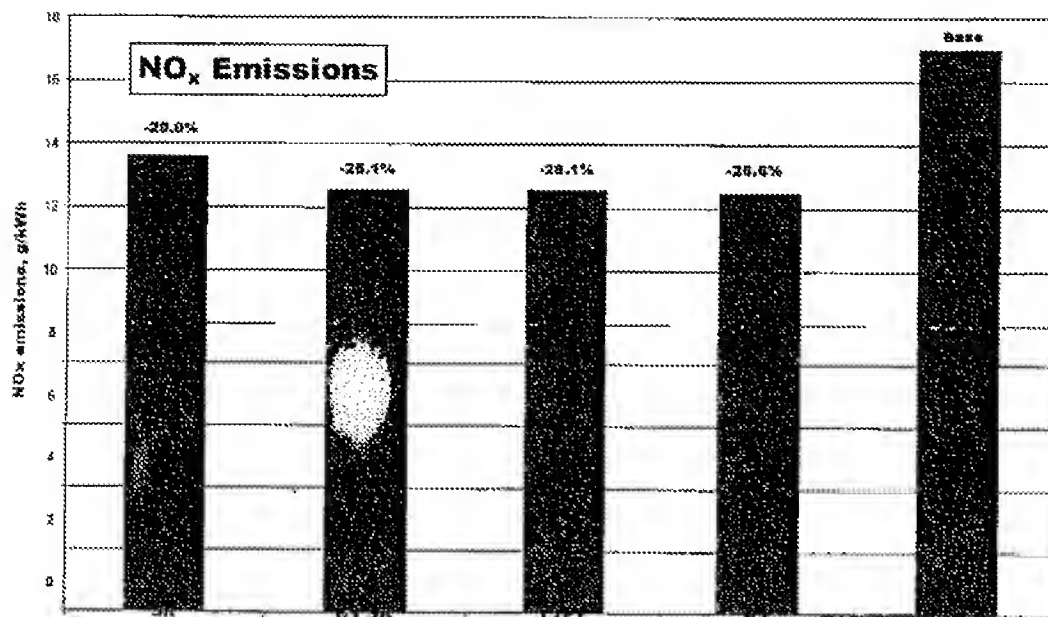
**Table 7: Fuel Characteristics of the Commercial Diesel-Synthetic Naphtha Blends**

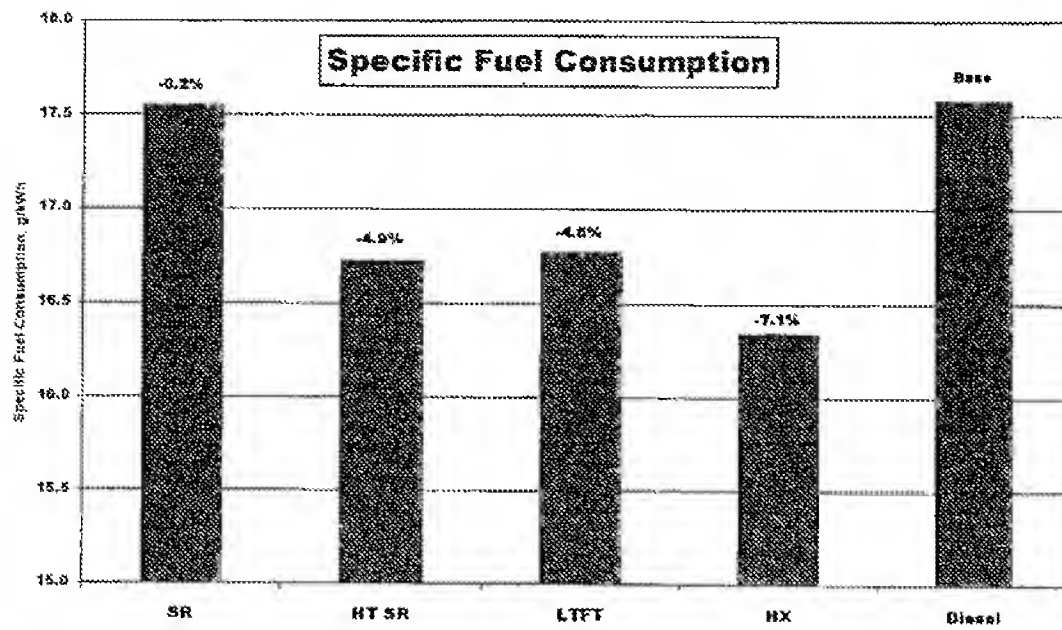
		LTFT Naphtha in Blend		
		0%	50%	100%
ASTM D86 Distillation °C	IBP	182	50	53
	T10	223	87	79
	T50	292	129	100
	T90	358	340	120
	FBP	382	376	129
Specific Gravity		0.8483	0.7716	0.6848
Flash Point	°C	77	47	-20
Viscosity	cSt 40°C	3.97	1.19	0.50
Cetane Number		50,0	41,8	39,6
Cloud Point (DSC)	°C	4	-5	-35
CFPP	°C	-6	-16	-40

**Table 8:** CI Engine and Emissions Performance of the Commercial Diesel-Synthetic Naphtha  
Blends

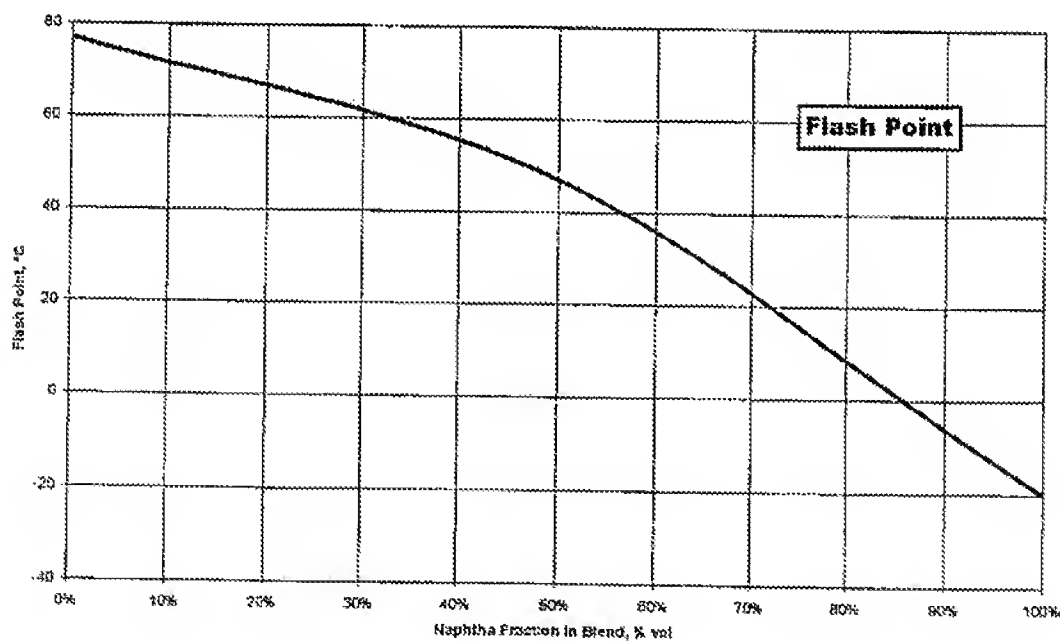
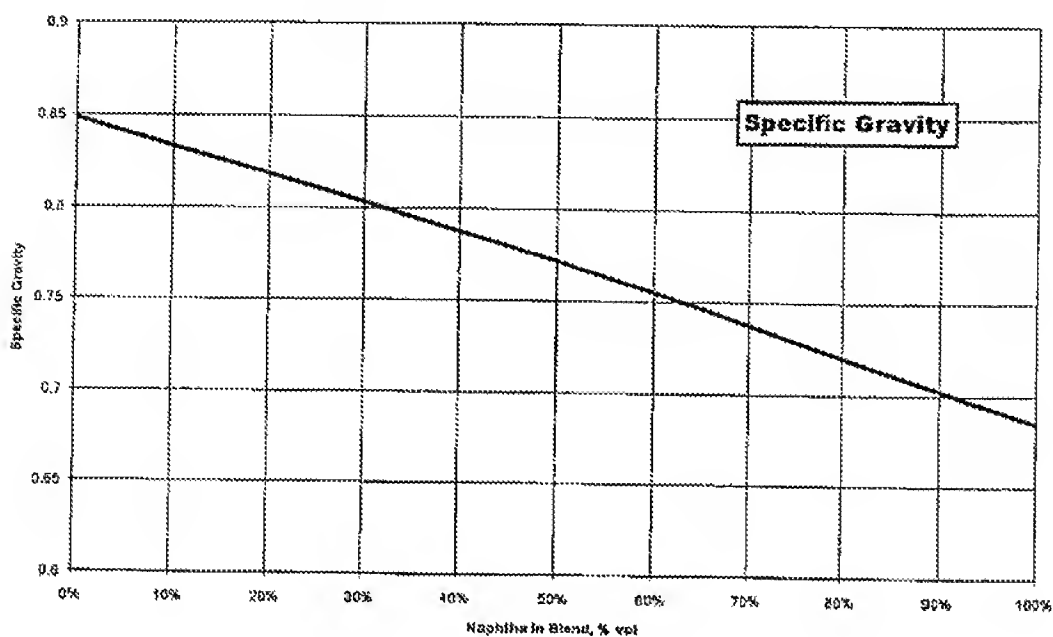
	LTFT Naphtha in Blend		
	0%	50%	100%
Engine tested	Mercedes Benz 407T		
Test condition	1 400 rpm		
Engine load	553 Nm		
Fuel Consumption, kg/h	17,58	16,71	16,77
Emissions			
CO, g/kWh	1,11	1,21	0,83
CO <sub>2</sub> , g/kwh	700,9	711,6	670,1
NO <sub>x</sub> , g/kwh	16,99	13,85	12,55
Bosch Smoke Number	0,67	0,53	0,37

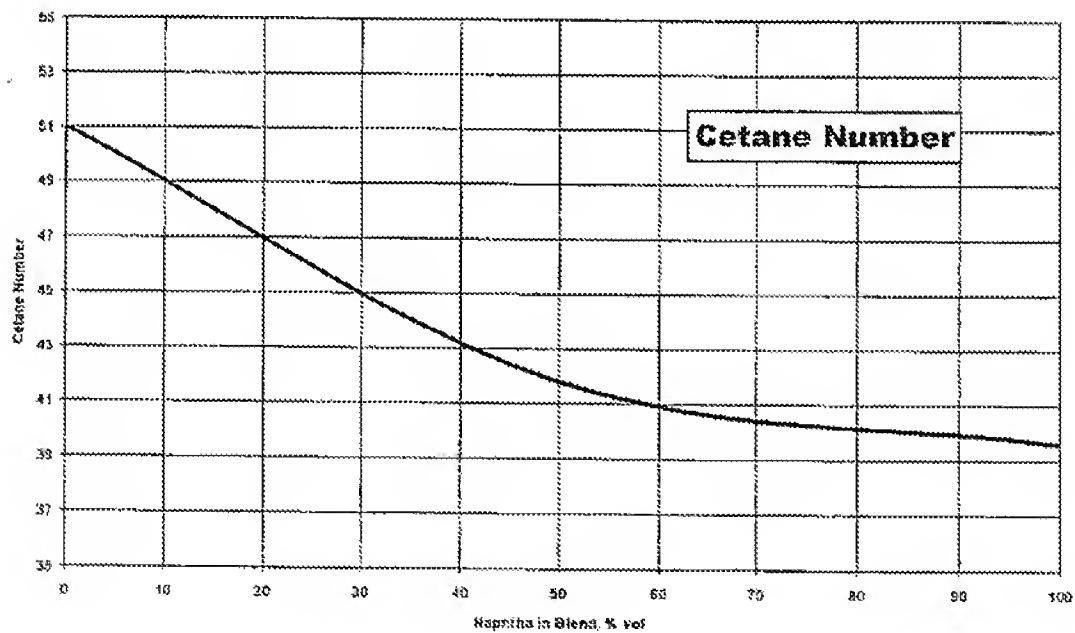
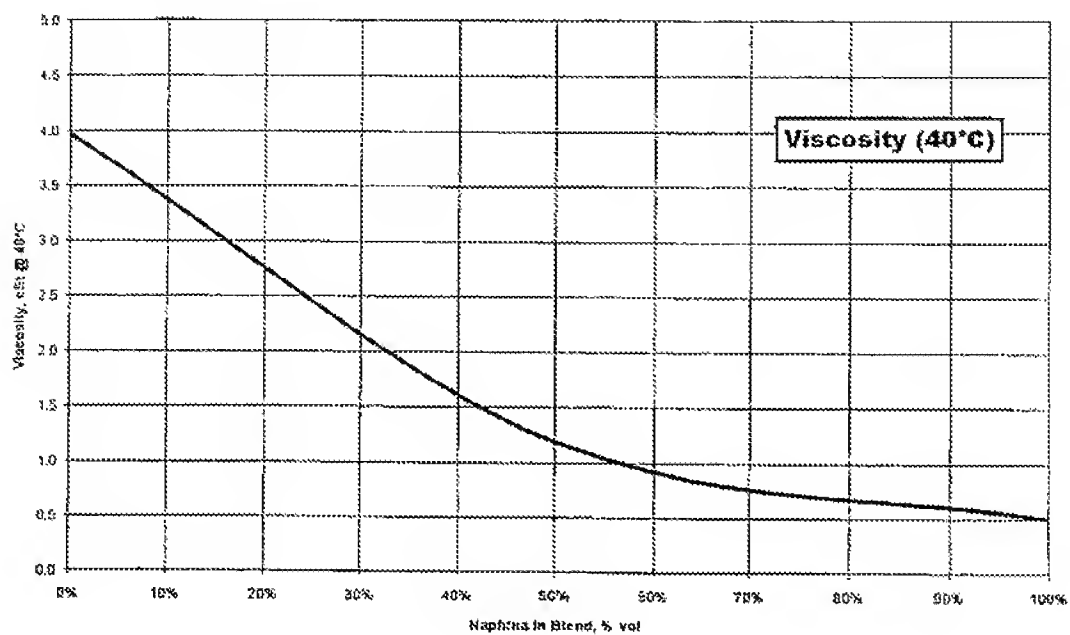
**Combustion and Emissions Performance of the Synthetic Naphthas**





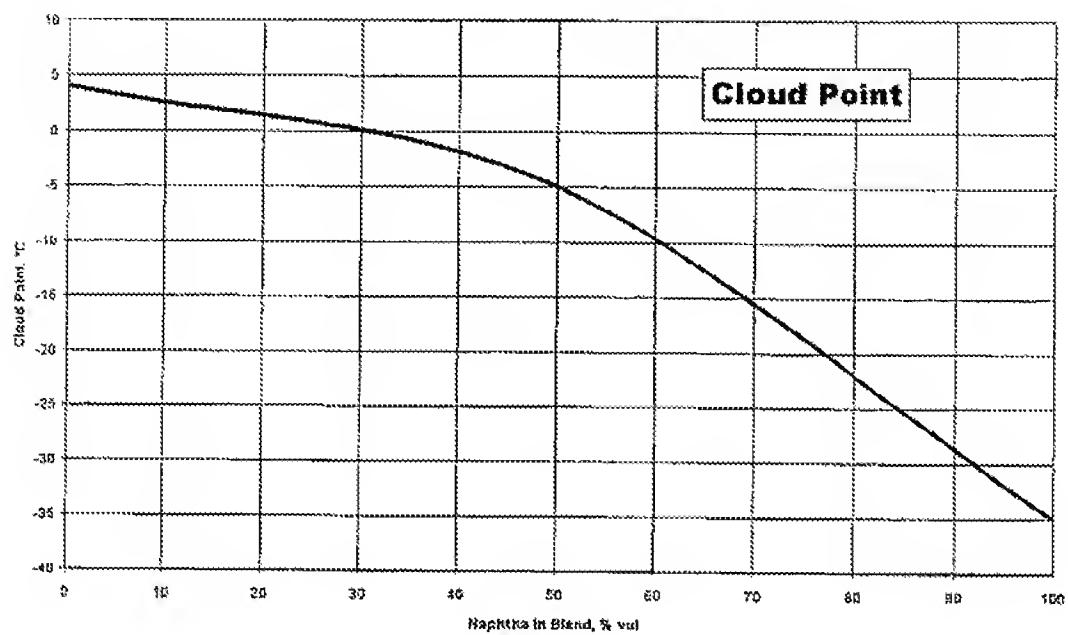
### Combustion and Emissions Performance of the LTFT Synthetic Naphtha and Commercial Diesel Blend





5

10



5

## Claims:

1. A process for the production of a synthetic naphtha fuel suitable for use in CI engines, the process including at least the steps of:

- a) hydrotreating at least a fraction of a Fischer-Tropsch (FT) synthesis reaction product of CO and H<sub>2</sub>, or a derivative thereof;
- b) hydrocracking at least a fraction of the FT synthesis product or a derivative thereof; and
- c) fractionating the process products to obtain a desired synthetic naphtha fuel characteristic.

2. A process as claimed in claim 1, which includes the additional step of blending the fractionated process products in a desired ratio to obtain a synthetic naphtha fuel having desired characteristics for use in a CI engine.

3. A process as claimed in claim 1 or claim 2, which produces a synthetic naphtha having at least some desired characteristics including:

- having a high Cetane number in excess of 30;
- having low sulfur content below 5 ppm;
- having good cold flow properties; and
- having more than 30% isoparaffins, wherein the isoparaffins are predominantly methyl branched.

4. A process for producing a synthetic naphtha fuel having a Cetane number higher than 30, the process including:

- (a) separating the products obtained from synthesis gas via the FT synthesis reaction into one or more heavier fraction and one or more lighter fraction;
- (b) catalytically processing the heavier fraction under conditions which yield predominantly distillates;
- (c) separating a naphtha product fraction of step (b) from a heavier product fraction which is also produced in step (b); and
- (d) optionally, blending the naphtha product obtained in step (c) with at least a portion of the one or more lighter fraction of step (a), or products thereof.

5. A process as claimed in claim 4, wherein the catalytic processing of step (b) is a hydroprocessing step.

6. A process as claimed in claim 5, wherein the hydroprocessing step includes hydrocracking.

7. A process as claimed in any one of claims 4 to 6, including one or more additional step of fractionating at least some of the one or more lighter fraction of step (a), or products thereof, prior to step (d).

5 8. A process as claimed in any one of claims 4 to 7, including the additional step of hydrotreating at least some of the one or more light fraction of step (a), or products thereof, prior to step (d).

9. A process as claimed in any one of claims 4 to 8, wherein the one or more heavier fraction of step (a) has a true boiling point (TBP) in the range of about 70°C to 700°C.

10

10. A process as claimed in any one of claims 4 to 8, wherein the one or more heavier fraction of step (a) has a true boiling point (TBP) in the range 80°C to 650°C.

11. A process as claimed in any one of claims 4 to 10, wherein the one or more lighter fraction has  
15 a true boiling point (TBP) in the range -70°C to 350°C.

12. A process as claimed in any one of claims 4 to 10, wherein the one or more lighter fraction has a true boiling point (TBP) in the range -10°C to 340°C.

13. A process as claimed in any one of claims 4 to 12, wherein the product of step (d) boils in the range 30°C to 200°C, as measured by the ASTM D86 method.

14. A process as claimed in any one of claims 4 to 12, wherein the product of step (d) boils in the range 40°C to 155°C, as measured by the ASTM D86 method.

25

15. A process as claimed in any one of claims 4 to 14, wherein the product of step (d) is a naphtha fuel.

16. A process as claimed in any one of claims 4 to 15, wherein the product of step (d) has a Cloud  
30 Point below -30°C.

17. A process as claimed in any one of claims 4 to 15, wherein the product of step (d) has a Cloud Point below -50°C.

18. A process as claimed in any one of claims 4 to 17, wherein the product of step (d) is obtained by mixing the naphtha product fraction obtained in step (c) with at least a portion of the one or more lighter fraction of step (a), or products thereof, in a volume ratio of between 1:24 and 9:1.

19. A process as claimed in any one of claims 4 to 17, wherein the product of step (d) is obtained by mixing the naphtha product fraction obtained in step (c) with at least a portion of the one or more lighter fraction of step (a), or products thereof, in a volume ratio of between 2:1 and 6:1.

5

20. A process as claimed in any one of claims 4 to 17, wherein the product of step (d) is obtained by mixing the naphtha product fraction obtained in step (c) with at least a portion of the one or more lighter fraction of step (a), or products thereof, in a volume ratio of 1:1.

10 21. A process for the production of synthetic naphtha fuels suitable for CI engines, from FT primary products, comprising predominantly short chain linear and branched paraffins.

22. A process as claimed in claim 21, wherein waxy product from a FT process is separated into at least two fractions, a heavier and at least one lighter fraction, the lighter fraction is subjected to mild  
15 catalytic hydrogenation to remove hetero-atomic compounds such as oxygen and to saturate olefins, thereby producing material useful as naphtha, diesel, solvents, and/or blending components therefor.

23. A process as claimed in claim 22, wherein the heavier fraction is catalytically hydroprocessed without prior hydrotreating to produce products with good cold flow characteristics.

20

24. A process as claimed in claim 23, wherein the hydroprocessed heavier fraction is blended with all or part of the hydrogenated and/or unhydrogenated light fraction to obtain, after fractionation, naphtha fuel characterised by an acceptable Cetane number.

25 25. A process for the production of a synthetic fuel suitable for use in CI engines, the process including at least the step of blending a synthetic naphtha fuel with a diesel fuel.

26. A process as claimed in claim 25, wherein the naphtha fuel and diesel fuel are blended in substantially equal proportions (v/v).

30

27. A process as claimed in claim 25 or claim 26, wherein the synthetic naphtha fuel is produced according to a process as claimed in any one of claims 1 to 24.

28. A synthetic naphtha fuel having a Cetane number above 30 and a Cloud Point, of below -  
35 30°C, said naphtha fuel having more than 30% isoparaffins, wherein the isoparaffins are predominantly methyl branched.

29. A synthetic naphtha fuel as claimed in claim 28 being a FT product.

30. A fuel composition including from 1% to 100% of a synthetic naphtha fuel as claimed in claim 28 or claim 29.

5

31. A fuel composition as claimed in claim 30, which includes from 0 to 99% of one or more diesel fuels.

10

32. A fuel composition as claimed in claim 30 or claim 31, which includes at least 20% of the synthetic naphtha fuel, the composition having a Cetane number greater than 40 and a Cloud Point below 2°C.

15

33. A fuel composition as claimed in claim 30 or claim 31, which includes at least 30% of the synthetic naphtha fuel, the composition having a Cetane number greater than 40 and a Cloud Point below 0°C.

20

34. A fuel composition as claimed in claim 30 or claim 31, which includes at least 50% of the synthetic naphtha fuel, the composition having a Cetane number greater than 40 and a Cloud Point below -4°C.

35. A fuel composition as claimed in claim 30 or claim 31, which includes at least 70% of the synthetic naphtha fuel, the composition having a Cetane number greater than 40 and a Cloud Point below -13°C.

25

36. A fuel composition as claimed in claim 31, which includes equal volumes of the synthetic naphtha fuel and the diesel fuel.

37. A fuel composition as claimed in claim 36, which has a Cetane number greater than 40 and a Cloud Point below -5°C.

30

38. A fuel composition as claimed in any one of claims 30 to 36, which further includes from 0 to 10% additives to improve other fuel characteristics.

35

39. A fuel composition as claimed in any one of claims 31 to 38, which includes as the diesel, a crude oil derived diesel.

40. A fuel composition as claimed in claim 39, wherein the crude oil derived diesel is selected from the group consisting of US 2-D grade (low sulphur No. 2-D grade for diesel fuel oil as specified in ASTM D 975-94) and CARB (California Air Resources Board 1993 specification) diesel fuel.

41. A fuel composition as claimed in claim 39, wherein the crude oil derived diesel is a commercial diesel from South Africa.

42. A Cloud Point depressant for a diesel fuel containing fuel composition, the Cloud Point depressant including predominantly synthetic naphtha.

43. A Cloud Point depressant as claimed in claim 42, the Cloud Point depressant providing at least a 2°C depression in Cloud Point for the fuel composition when present in the fuel composition in a ratio of synthetic naphtha to diesel fuel of at least 1:4.

44. A Cloud Point depressant as claimed in claim 42, the Cloud Point depressant providing at least a 8°C depression in Cloud Point for the fuel composition when present in the fuel composition in a ratio of synthetic naphtha to diesel fuel of at least 1:1.

45. A Cloud Point depressant as claimed in claim 42, the Cloud Point depressant providing at least a 18°C depression in Cloud Point for the fuel composition when present in the fuel composition in a ratio of synthetic naphtha to diesel fuel of at least 7:3.

46. A Cloud Point depressant as claimed in any one of claims 42 to 45, which is at least 95% synthetic naphtha.

47. A Cloud Point depressant as claimed in any one of claims 42 to 46, which is at least 99% synthetic naphtha.

48. A fuel composition as claimed in any one of claims 30 to 39, the performance of which when used in a CI engine results in at least 25% lower NO<sub>x</sub> emissions compared with a conventional diesel fuel tested under the same conditions.

49. A fuel composition as claimed in any one of claims 30 to 39, the performance of which when used in a CI engine results in at least 45% lower Particulates emission measured by the Bosch Smoke Number emissions compared with a conventional diesel fuel tested under the same conditions.

50. A synthetic naphtha as claimed in any one of claims 28 to 29, the performance of which when used in a CI engine results in at least 4% lower specific fuel consumption (kg/h) compared with a conventional diesel fuel tested under the same conditions.

5 51. A fuel composition as claimed in any one of claims 30 to 39, the performance of which when used in a CI engine results in at least 19% lower NO<sub>x</sub> emissions compared with a conventional diesel fuel tested under the same conditions.

10 52. A fuel composition as claimed in any one of claims 30 to 39, the performance of which when used in a CI engine results in at least 21% lower Particulates emission measured by the Bosch Smoke Number emissions compared with a conventional diesel fuel tested under the same conditions.

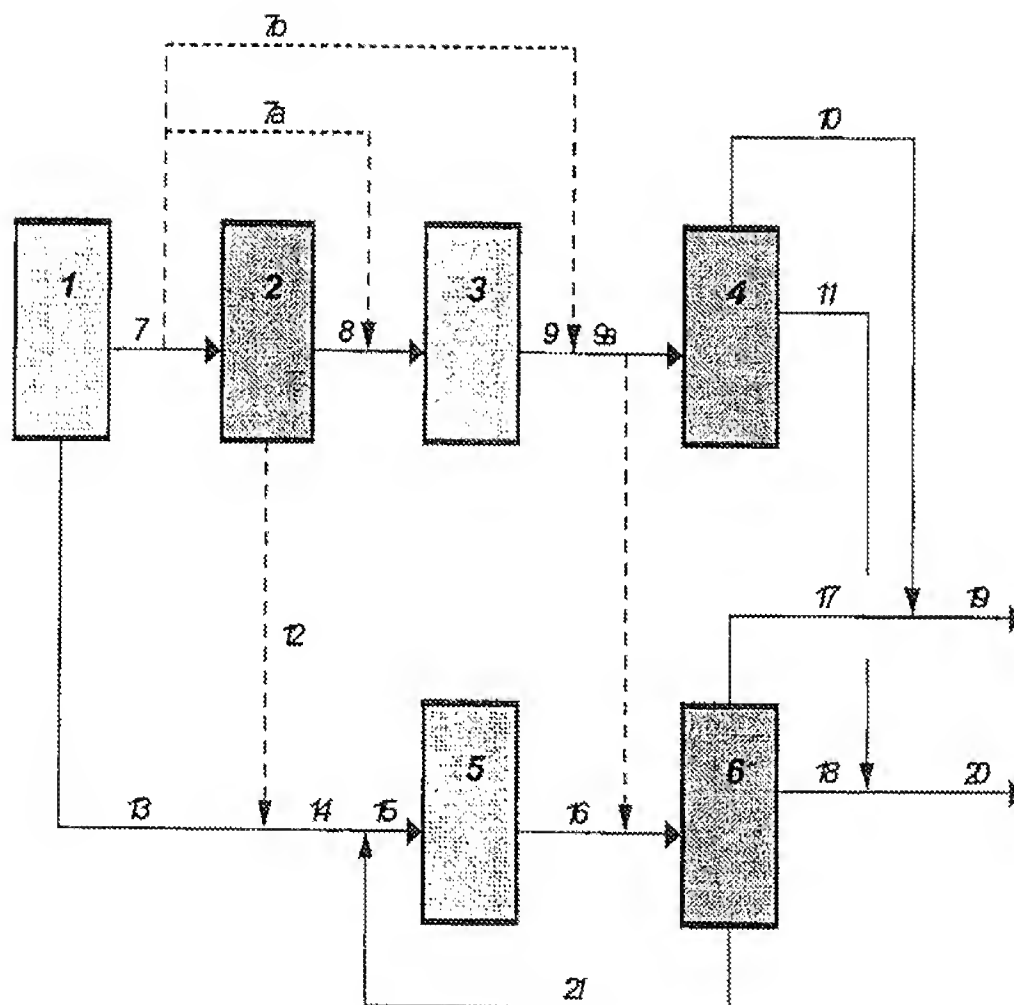
15 53. A fuel composition as claimed in any one of claims 30 to 39, the performance of which when used in a CI engine results in at least 10% lower specific fuel consumption (kg/h) compared with a conventional diesel fuel tested under the same conditions.

20 54. A synthetic naphtha as claimed in any one of claims 28 to 29, the performance of which when used in a CI engine results in at least 25% lower CO emissions compared with a conventional diesel fuel tested under the same conditions.

25 55. A synthetic naphtha as claimed in any one of claims 28 to 29, the performance of which when used in a CI engine results in at least 4% lower CO<sub>2</sub> emissions compared with a conventional diesel fuel tested under the same conditions.

1/1

Figure 1



## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/ZA 99/00147

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10L1/08 C10G65/14 C10G2/00 C10L1/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G C07C C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 30 30 998 A (METALLGESELLSCHAFT AG) 1 April 1982 (1982-04-01) claim 1 example 1 figure 1 ---	1,6, 9-11,15
A	US 5 378 348 A (DAVIS STEPHEN M ET AL) 3 January 1995 (1995-01-03) cited in the application ---	
X	EP 0 532 116 A (SHELL INT RESEARCH) 17 March 1993 (1993-03-17) claims 1,15,16 column 9, line 51 -column 10, line 5 examples 1,2 ---	4-7,9, 10,13-15
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

14 July 2000

Date of mailing of the international search report

22.08.00

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2200 HV Rijswijk  
Tel: (+31-70) 340-2040, Tx. 31 651 epo.nl  
Fax: (+31-70) 340-3016

Authorized officer

De Herdt, O

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/ZA 99/00147

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 814 109 A (COOK BRUCE R ET AL) 29 September 1998 (1998-09-29)	25, 26, 28-33, 36-39
A	claims 1, 5, 6 column 1, line 6 - line 10 table 1E	27
E	WO 00 20535 A (DANCUART LUIS PABLO ;WET EWALD WATERMEYER DE (ZA); HAAN ROBERT DE) 13 April 2000 (2000-04-13) claims 1, 2, 27, 40, 43, 54	21-24
X	US 5 645 613 A (YAKOBSON DENNIS L ET AL) 8 July 1997 (1997-07-08) claim 1 column 21, line 19 - line 38	25, 27
X	BE 459 498 A (LINDEMANN ET.AL) claims 1, 7	25, 26

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/ZA 99/00147

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

As a result of the prior review under R. 40.2(e) PCT,  
no additional fees are to be refunded.

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☒ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International Application No. PCT/ZA 99 00147

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1,2,3,

6 (partially as far as related to hydrocracking)  
and 7-20 as far as dependent on 6,  
8 (partially as far as related to hydrotreating)  
and 9-20 as far as dependent on 8 and its  
dependent claims 23 and 24 ,  
22 ( as far as related to hydrotreating),  
27 ( as far as dependent on claim 1)

I The independent claim 1 describes a process for the production of synthetic naphtha for use in a CI-engine by a combination process of hydrotreating and hydrocracking of Fischer-Tropsch products.

2. Claims: 4 and its dependent claims 5-20,

23 (as far as related to the catalytic  
hydroprocessing) and its dependent claim 24,  
27 (as far as dependent on claims 4,23 and 24,  
28 and its dependent claims 29-41 and 48-51.

II The independent claim 4 describes a process for the production of synthetic naphtha by catalytic processing of Fischer-Tropsch products, followed by separating and optionally a blending operation and the synthetic naphtha fuel as described in claim 28.

The synthetic naphtha is characterised by a cetane number higher than 30, a cloud point less than 30 C and an isoparaffins content of at least 30%, the isoparaffins being predominantly monomethylbranched.

3. Claims: 21 and its dependent claims 22-24.

III The independent claim 21 describes a process for the production of synthetic naphtha, for use in a CI-engine, comprising short chain linear and branched paraffins.

4. Claims: 25 and its dependent claims 26 and 27,42-47

IV The independent claim 25 describes a process for the production of synthetic fuel by blending synthetic naphtha with diesel.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/ZA 99/00147

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3030998 A	01-04-1982	AU 7409381 A ZA 8104282 A	25-02-1982 28-07-1982
US 5378348 A	03-01-1995	AU 671224 B AU 6862194 A CA 2127010 A DE 69423148 D DE 69423148 T EP 0635557 A NO 942726 A	15-08-1996 02-02-1995 23-01-1995 06-04-2000 13-07-2000 25-01-1995 23-01-1995
EP 0532116 A	17-03-1993	AU 653856 B AU 2350092 A CA 2077942 A DE 69229313 D DE 69229313 T FI 924052 A JP 5302088 A NO 304273 B	13-10-1994 18-03-1993 13-03-1993 08-07-1999 18-11-1999 13-03-1993 16-11-1993 23-11-1998
US 5814109 A	29-09-1998	BR 9807171 A EP 0958334 A NO 993739 A WO 9834998 A ZA 9800621 A	25-01-2000 24-11-1999 07-10-1999 13-08-1998 22-07-1998
WO 0020535 A	13-04-2000	AU 6300199 A	26-04-2000
US 5645613 A	08-07-1997	US 5324335 A US 5543437 A US 5621155 A US 5620670 A US 5763716 A AU 6028894 A WO 9520558 A US 5504118 A US 5506272 A US 5500449 A	28-06-1994 06-08-1996 15-04-1997 15-04-1997 09-06-1998 15-08-1995 03-08-1995 02-04-1996 09-04-1996 19-03-1996
BE 459498 A		NONE	